NON-CERTIFIED, UNFORMATTED TRANSLATION FROM INTERLINGUA.COM

Reference No.
Job No. TOT-LYON-2268A

19. Japan Patent Office (JP) 11. Patent Application Laid-open No.

12. Japan Laid-open Patent Gazette (A) Showa 62-117330(1987)

51. Int. Cl.[5]	ID Code	Internal Reference No.	43. Patent Laid-open Date: May 28, 1987 (Showa 62)
H 01 LJ 21/304		D-7446-4F	Place for Technology Labeling
B 08 B 21/304		Z-6420-3B	

Request for Examination: Attached / Not Requested Number of Claims: 1 (Total 3 pages)

54. Title of Invention	Semiconductor Wafer Cleaning Method
21. Application No.	Showa 60-258064
22. Date of Filing	November 18, 1985 (Showa 60)
72. Inventor	Toshio Wada 18, Oaza-Sakada, Oizumi-cho, Ouragun, Gunma-ken Tokyo Sanyo Electric Co., Ltd
72. Inventor	Norio Koide 18, Oaza-Sakada, Oizumi-cho, Ouragun, Gunma-ken Tokyo Sanyo Electric Co., Ltd
71. Applicant	Sanyo Electric Co., Ltd 2-18, Keihan-hondori, Moriguchi-shi, Osaka
71. Applicant	Tokyo Sanyo Electric Co., Ltd 18, Oaza-Sakada, Oizumi-cho, Ouragun, Gunma-ken
74. Agent	Takushi [1]Nishino, Patent Attorney, and one additional person

Wada et al

SPECIFICATION

1. Title of the invention Semiconductor Wafer Cleaning Method

Immersion

2. Claims

(1) A semiconductor wafer cleaning method, characterized in that a semiconductor wafer is immersed in a cleaning liquid composed of ammonia, sulfuric acid, hydrochloric acid or other substance, whereupon ozone is supplied to the aforementioned cleaning liquid.

3. Detailed description of the invention

Field of industrial utilization

The present invention concerns a method for cleaning semiconductor wafers, and in particular, concerns a method for cleaning semiconductor wafers wherein oxygen is supplied during cleaning.

Prior art

In the past, methods for cleaning semiconductor wafers, as shown in Figure 2, have involved introducing a dilute solution containing 10% or less of such substances as sulfuric acid (H_2SO_4), aqueous ammonia (NH_4OH), hydrochloric acid (HCl) and hydrofluoric acid (HF) into a cleaning vessel 11, and heating this cleaning liquid 13 to approximately 80°C with a heater 12. The semiconductor wafer is cleaned by immersing it in this liquid 13. In order to improve the cleaning activity, hydrogen peroxide (H_2O_2) is added dropwise to the cleaning liquid 13 immediately prior to introduction of the semiconductor wafer so that oxygen is generated, thereby achieving greater cleaning uniformity.

heating clean sol

80°C + heater

[1] ILS Note – An alternative way of reading this person's name is Hiroshi.

InterLingua.com, Inc
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E-mail: interlingua@interlinguacom.com

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This type of method is common knowledge in, for example, Japanese Unexamined (Kokai) Patent Application No. Sho 59-46032 (H 01 L 21/304).

Problems to be solved by the invention

However, various disadvantages have resulted from the type of method described above. Firstly, there is the disadvantage that water is generated due to thermal decomposition resulting from the use of hydrogen peroxide, and the cleaning liquid 13 is thus additionally diluted, producing non-uniform cleaning which results in a loss of surface uniformity of the semiconductor wafer. For this reason, the defect density of oxide films formed by thermal oxidation increases, and the surface condition becomes non-uniform during polysilicon cleaning.

Secondly, there is the disadvantage that the cleaning liquid 13 is contaminated by contaminants contained in the liquid because hydrogen peroxide is used, so that a clean cleaning process is not carried out.

Thirdly, if the attempt is made to improve cleaning efficiency by increasing the temperature of the cleaning liquid 13, there is the disadvantage that thermal decomposition of the hydrogen peroxide will accelerate, and the cleaning effects will actually be compromised.

Means for solving the problems

The present invention was developed in light of the disadvantages described above, and offers a cleaning method for semiconductor wafers wherein past disadvantages have been dramatically mitigated by means of supplying ozone to the cleaning liquid.

Action

In accordance with the present invention, ozone gas is introduced into the cleaning liquid 4 during cleaning, so that oxygen can be supplied in constant quantities and dilution of the cleaning liquid 4 can be stopped.

Working examples

The cleaning method for semiconductor wafers pertaining to the present invention is described below in reference to Figure 1.

A 90-96% concentrated sulfuric acid stock solution (H_2SO_4), ammonia aqueous solution (NH_4OH), hydrochloric acid (HCl), nitric acid (HNO_3) or hydrofluoric acid (HF) is diluted to 10% or less and is introduced as cleaning liquid 4 into a cleaning vessel 1, where a pipe 2 composed of quartz or Teflon is installed below the cleaning vessel 1 in such a manner that ozone (O_3) is blown upwards from below. A heater 3 is installed below the cleaning vessel 1 for heating the cleaning liquid 4. With sulfuric acid, heating is performed at 100-140°C, whereas with ammonia aqueous solution, heating is performed at 80-100°C.

O_3 → heats 80-100

A semiconductor wafer that is held on a stand is immersed in this cleaning vessel 1, and ozone is introduced from the pipe 2 so that the semiconductor wafer is cleaned while supplying oxygen ions into the cleaning liquid 4.

In this method, oxygen ions are continuously supplied without accompanying dilution of the cleaning liquid 4 because ozone is a gas. By this means, oxidation of the cleaned surface is facilitated and a hydrophilic treatment is carried out, so that an extremely clean cleaning process can be performed with good reliability.

Characteristic curves used for representing cleaning effects in the cleaning method of the present invention and a conventional cleaning method are shown in Figure 3. In comparing the method of the present invention wherein $NH_4OH + O_3$ is used and a method known as a conventional RCA cleaning method wherein $NH_4OH + H_2O_2$ is used, the heating temperature has been restricted to 80-90°C in the past due to thermal decomposition of the H_2O_2, and the cleaning effects deteriorate as indicated by the arrow due to dilution of the liquid with water generated by thermal decomposition: H_2O_2 //arrow// H_2O + O*//upwards arrow//. With the present invention, however, ozone is used so that cleaning effects are greatly improved because heating can be performed at 100°C or greater. In addition, the method of the present invention that employs $H_2SO_4 + O_3$ provides effects that are similar to those of conventional methods that employ $H_2O_4 + H_2O_2$.

heat → improve clng effect

Effect of the invention

Firstly, the present invention has the advantage that ozone is used as the source for generating oxygen ions, so that the cleaning liquid 4 is not diluted, and cleaning is activated by the oxygen ions. As a result, cleaning can be reliably and uniformly carried out at the surface of the semiconductor wafer.

Secondly, the invention has the advantage that ozone is a gas, and thus there is no danger of pollution of the cleaning liquid 4 with contaminants when this substance is introduced, so that cleaning can be performed

without contamination.

Thirdly, the invention has the advantage that, because ozone is used, oxygen ions can be supplied in constant amounts even if the temperature of the cleaning liquid 4 is increased, because there is no connection with thermal degradation of H_2O_2. The cleaning effects can thus be increased by two or more times over past methods.

Fourthly, the invention has the advantage that, because ozone is used, H_2O_2 liquid need not be managed, which simplifies management from the standpoint of safety relative to cases where H_2O_2 is used.

Brief description of the figures

Figure 1 is a cross-sectional diagram describing the cleaning method for semiconductor wafers pertaining to the present invention, Figure 2 is a cross-sectional diagram describing a conventional method for cleaning semiconductor wafers, and Figure 3 is a graph for showing the cleaning effects obtained in the past and with the present invention.

1 Cleaning vessel
2 Pipe
3 Heater
4 Cleaning liquid

Figure 1

Figure 2

Figure 3
1 Cleaning effects (relative scale)
2 Temperature

AN - 87-117330
TI - WASHING METHOD FOR SEMICONDUCTOR WAFER
PA - ~~(2000188) SANYO ELECTRIC~~ CO LTD
IN - WADA, TOSHIO; KOIDE, NORIC
PN - ~~87.05.28 J62117330~~, JP 62-117330
AP - ~~85.11.18 85JP-258064~~, 60-258064
SO - 87.10.27 SECT. E, SECTION NO. 552; VOL. 11, NO. 329, PG. 141.
IC - H01L-021/304; B08B-003/10
JC - 42.2 (ELECTRONICS--Solid State Components); 28.1 (SANITATION--Sanitary Equipment)
AB - PURPOSE: To wash a wafer surface uniformly and stably without diluting a washing by injecting ozone gas into the washing during the washing time. CONSTITUTION: A diluted solution, such as 90-96% H(sub 2)SO(sub 4), NH(sub 4)OH, HCl, etc. is introduced into a washing tank 1 as a washing

4

while a pipe 2 consisting of quartz, Teflon, etc. with a large number of holes is mounted to a lower section in the tank 1 and ozone can be fed.

A

heater 3 is installed to the lower section of the tank 1, and the liquid 4 is heated. Semiconductor wafers housed in a jig are dipped into the tank 1, ozone is injected from the pipe 2, and the semiconductor wafers are washed, feeding oxygen ions to the liquid 4. Accordingly, since

ozone

is a gas, the liquid 4 is not diluted, and the oxidation of a washing surface is accelerated and hydrophilic treatment is executed, thus

stably

conducting extremely clean washing.

SS 24?

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Wada et. al

get

$H_2SO_4 - H_2O - O_3$
$NH_4OH - H_2O - O_3$ or
$HCl - H_2O - O_3$ or

-9- (WPAT)
AN - 87-188360/27
TI - Appts. for cleaning semiconductor wafer - supplies ozone into washings composed of ammonia, sulphuric acid, and hydrochloric acid during cleaning NoAbstract Dwg 1/3
DC - L03 P43 U11
PA - (SAOL) SANYO ELECTRIC CO; (TOKR) TOKYO SANYO ELECTRIC CO
PR - 85.11.18 85JP-258064
NUM - 1 patent(s) 1 country(s)
PN -- JP62117330 A 87.05.28 1 (8727) 8p
AP -- 85JP-258064 85.11.18
IC2 - B08B-003/10 H01L-021/30

102 - 82-85, 88-90

no rotating

⑲日本国特許庁(JP)　⑪特許出願公開

⑫公開特許公報(A)　昭62-117330

(51)Int.Cl.4　識別記号　庁内整理番号　㊸公開　昭和62年(1987)5月28日

H 01 L 21/304　D-7376-5F
B 08 B 3/10　Z-6420-3B

審査請求　未請求　発明の数 1　(全3頁)

(54)発明の名称　半導体ウエハの洗浄方法

㉑特　願　昭60-258064
㉒出　願　昭60(1985)11月18日

(72)発明者　和田　俊男　群馬県邑楽郡大泉町大字坂田180番地　東京三洋電機株式会社内
(72)発明者　小出　典男　群馬県邑楽郡大泉町大字坂田180番地　東京三洋電機株式会社内
(71)出願人　三洋電機株式会社　守口市京阪本通2丁目18番地
(71)出願人　東京三洋電機株式会社　群馬県邑楽郡大泉町大字坂[illegible]0番地
(74)代理人　弁理士　西野　卓嗣　外1名

明　細　書

1. 発明の名称　半導体ウェハの洗浄方法

2. 特許請求の範囲

(1) アンモニア、硫酸、塩酸等より成る洗浄液内に半導体ウェハを浸漬した後、前記洗浄液中にオゾンを供給することを特徴とする半導体ウェハの洗浄方法。

3. 発明の詳細な説明

(イ) 産業上の利用分野

本発明は半導体ウェハの洗浄方法、特に洗浄中に酸素を供給する半導体ウェハの洗浄方法に関する。

(ロ) 従来の技術

従来、半導体ウェハの洗浄方法としては第2図に示す如く、洗浄槽(11)内に硫酸(H_2SO_4)、アンモニア水(NH_4OH)、塩酸(HCℓ)、弗酸(HF)等の10%以下の希釈液を洗浄液(13)として入れ、この洗浄液(13)をヒーター(12)で約80℃程度に加熱し、この液(13)内に半導体ウェハを浸漬して洗浄を行っている。洗浄の活性化を行うために半導体ウェハへの投入直前に過酸化水素(H_2O_2)を洗浄液(13)に滴下して酸素を発生させて洗浄の均一化を図っている。

斯る方法は例えば特開昭59-46032号公報(H01L21/304)等で公知である。

(ハ) 発明が解決しようとする問題点

しかしながら斯上の方法では種々の欠点が生じた。第1に過酸化水素を用いるため熱分解されて水が発生し、洗浄液(13)が更に希釈され洗浄にむらが生じて半導体ウェハの表面均一性が悪い欠点があった。このため熱酸化による酸化膜の欠陥密度が高くなったり、ポリシリコンの洗浄では表面状態にむらが生じる。

第2に過酸化水素を用いるためその液内に含まれるゴミで洗浄液(13)が汚れ、クリーンな洗浄を行なえない欠点があった。

第3に洗浄液(13)の温度を上昇して洗浄効率を上げようとすると過酸化水素の熱分解が速められてかえって洗浄効果が落ちる欠点があった。

(ニ) 問題点を解決するための手段

本発明は斯上した欠点に鑑みてなされ、洗浄液中にオゾンを供給することにより従来の欠点を大巾に改善した半導体ウェハの洗浄方法を提供するものである。

(ホ) 作用

本発明に依れば、洗浄時間中洗浄液(4)中にオゾンガスを注入しているので、酸素を一定量供給でき洗浄液(4)の希釈化も防止できる。

(ヘ) 実施例

本発明に依る半導体ウェハの洗浄方法を第1図を参照して詳述する。

洗浄槽(1)内に90〜96%の濃硫酸原液（H_2SO_4）、アンモニア水（NH_4OH）、塩酸（HCl）、硝酸（HNO_3）、弗酸（HF）等の10%以下の希釈液を洗浄液(4)として入れ、この洗浄槽(1)下に多孔を有する石英又はテフロンより成るパイプ(2)を設けてオゾン（O_3）が下から吹き出す様になっている。洗浄槽(1)の下にはヒーター(3)を設け、洗浄液(4)を加熱する。硫酸の場合は100〜140℃に加熱し、アンモニア水の場合は80〜100℃に加熱している。

斯る洗浄槽(1)内に治具に収納した半導体ウェハを浸漬し、パイプ(2)よりオゾンを注入して酸素イオンを洗浄液(4)内に供給しながら半導体ウェハの洗浄を行う。

斯る方法に依れば、オゾンが気体であるので洗浄液(4)の希釈化を伴なわずに酸素イオンを供給し続ける。これにより洗浄表面の酸化を促進して親水処理を行なえるので極めてクリーンな洗浄を安定して行なうことができる。

第3図に本発明と従来の洗浄方法の洗浄効果を説明する特性図を示す。従来RCA洗浄法と呼ばれている$NH_4OH+H_2O_2$と本発明のNH_4OH+O_3とを比較すると、従来では加熱温度がH_2O_2の熱分解より80〜90℃に限られ、$H_2O_2 \rightarrow H_2O+O^{*}\uparrow$の熱分解により発生する水により液希釈が生じて矢印の様に洗浄効果が劣化しているのに対し、本発明ではオゾンを用いるため100℃以上に加熱でき洗浄効果を大巾に向上できる。また従来の$H_2SO_4+H_2O_2$と本発明の$H_2SO_4+O_3$についても同様の効果が得られる。

(ト) 発明の効果

本発明に依れば、第1にオゾンを酸素イオン発生部として用いるので洗浄液(4)が希釈化されず、酸素イオンで洗浄が活性化され半導体ウェハの表面を均一に且つ安定して洗浄できる利点を有する。

第2にオゾンは気体であるので注入しても洗浄液(4)がゴミ等で汚染されるおそれがなくなり、クリーンな洗浄ができる利点を有する。

第3にオゾンを用いるので洗浄液(4)の温度をH_2O_2の熱分解に無関係に上げても酸素イオンを一定量供給でき、洗浄効果を従来の2倍以上に向上できる利点を有する。

第4にオゾンを用いるのでH_2O_2を用いる場合に比べてH_2O_2の液の管理が不要となり安全上の管理が容易となる利点を有する。

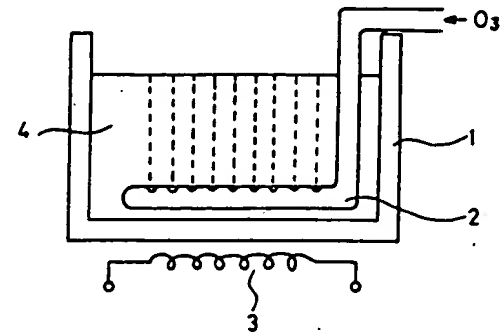
4. 図面の簡単な説明

第1図は本発明に依る半導体ウェハの洗浄方法を説明する断面図、第2図は従来の半導体ウェハの洗浄方法を説明する断面図、第3図は本発明と従来の洗浄効果を説明する曲線図である。

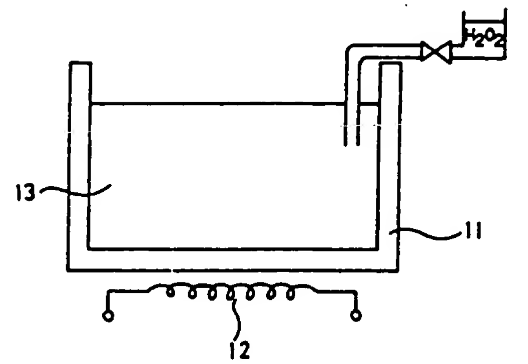
(1)は洗浄槽、(2)はパイプ、(3)はヒーター、(4)は洗浄液である。

出願人　三洋電機株式会社　外1名
代理人　弁理士　佐野静夫

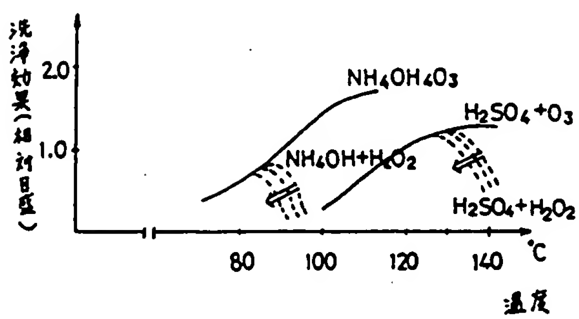
第1図


O3
4
1
2
3

第2図


H2O2
13
11
12

第3図


洗浄効果(相対目盛)
2.0
1.0
NH4OH+O3
H2SO4+O3
NH4OH+H2O2
H2SO4+H2O2
80
100
120
140
°C
温度

19. Japan Patent Office (JP) **12. Japan Laid-open Patent Gazette (A)** 11. Patent Application Laid-open No.

Heisei 8-160032 (1996)

43. Patent Laid-open Date: June 21, 1996 (Heisei 8)

51. Int. Cl.[6]		ID Code	Internal Reference No.	FI	Place for Technology Labeling
C 01 N	33/00	A			
	31/00	Y			
H 01 L	21/66	L	7735-4M		Fukazawa

Request for Examination: Not Requested Number of Claims: 4 OL (Total 4 pages)

21. Application No. Heisei 6-303375

22. Date of Filing December 7, 1994 (Heisei 6)

71. Applicant 000003078
TOSHIBA Corporation
72, Horikawa-cho, Saiwai-ku, Kawasaki-shi, Kanagawa-ken

72. Inventor Yuji Fukazawa
Research and Development Center, TOSHIBA Corporation.
1, Komukai-Toshiba-cho, Saiwai-ku, Kawasaki-shi, Kanagawa-ken

74. Agent Kenyu[1] Norichika, Patent Attorney

54. Title of the Invention

A Method of Analyzing Impurities on the Surface of Semiconductor Substrate

(54) [Title of Invention] A Method of Analyzing Impurities on the Surface of Semiconductor Substrate

(57) [Summary]
[Purpose] The purpose of the invention is to analyze the impurities present on the surface of semiconductor substrate with high degree of precision and sensitivity.
[Composition] Aqueous solution or vaporized HF is supplied from line 15, and aqueous solution or gaseous O_3 is supplied from line 16 to form a dissolving solution 17 of HF and O_3 on the surface of semiconductor substrate 12. The semiconductor substrate 12 is put in motion, such as rotation, by a driving mechanism 14 causing the dissolving solution 17 to roll on the surface of the semiconductor substrate 12. Consequently, the impurity present on the surface of the semiconductor substrate 12 is dissolved by the dissolving solution 17. The dissolving solution 17 is then collected by a pipette, and analyzed by a flameless atomic absorption apparatus. By having HF and O_3 contained in the dissolving solution 17, oxide film is efficiently formed on the semiconductor substrate surface 12 by the oxidation power of O_3. The impurity on the semiconductor substrate surface is incorporated into the oxide film. The oxide film is then dissolved by the dissolving power of HF without etching the semiconductor substrate 12. Consequently, the type and quantity of the impurity adhered to the surface of semiconductor substrate 12 can be measured with high degree of accuracy and sensitivity.
[Scope of Patent Claims]
[Claim 1] A method of analyzing impurity on the semiconductor substrate surface comprises; a processing step to create a dissolving solution containing HF and O_3 on the surface of semiconductor substrate, and a processing step to roll the solution on the semiconductor substrate surface to make contact. It also comprises a processing step to analyze said dissolving solution to measure the type and quantity of the impurity adhered to the semiconductor substrate surface. These are the characteristics of the method of analyzing impurity on the semiconductor substrate surface.

[1] ILC Note – An alternative way of reading this name is "Norisuke."

[Claim 2] The dissolving solution containing HF and O_3, mentioned above, is created by mixing gaseous O_3 with either aqueous solution of HF or vaporized HF. These are the additional characteristics of the method of analyzing impurity on the semiconductor substrate surface described in Claim 1 of the Scope of Patent Claims.

[Claim 3] The dissolving solution containing HF and O_3, mentioned above, is created by mixing aqueous solution of O_3 with either aqueous solution of HF or vaporized HF. These are the additional characteristics of the method of analyzing impurity on the semiconductor substrate surface described in Claim 1 of the Scope of Patent Claims.

[Claim 4] A method of analyzing impurity on the semiconductor substrate surface comprises; a processing step to drip a dissolving solution containing HF and O_3 on the surface of semiconductor substrate, and a processing step to roll the solution on the semiconductor substrate surface to make contact. It also comprises a processing step to analyze said dissolving solution to measure the type and quantity of the impurity adhered to the semiconductor substrate surface. These are the characteristics of the method of analyzing impurity on the semiconductor substrate surface.

[Detailed Explanation of the Invention]

[0001]

[Areas of Industrial Application] This invention relates to a method of analysis that measures the type and quantity of impurities adhered to the surface of semiconductor substrate.

[0002]

[Prior Art] Higher level of performances, such as higher degree of integration, higher speed, greater number of functions, and higher reliability, are always demanded of ICs. To solve these issues, multitude of technologies have been introduced into hundreds of production work steps employed in the production of IC. One such technology is a technology to prevent impurities from entering the semiconductor substrate, composed of silicon (SI) as raw material, prior to the work step producing a device. As well known, prevention of impurities from entering the semiconductor substrate is indispensable in improving the device characteristics of ICs. To realize this objective, accurate analysis of the degree of contamination on the surface of semiconductor substrate is necessary.

[0003] Generally, the impurities entering the semiconductor substrates include organic substances, gas impurities, and metals. As a means of analyzing primarily metal, a method of measuring the type and quantity of impurities using a flameless atomic absorption apparatus is well known. In this method, the impurities adhered to the surface of semiconductor substrate and the impurities contained in a natural oxide film formed on the surface of semiconductor are dissolved with HF vapor. The dissolving solution is then collected to measure the type and quantity of the impurities contained with the flameless atomic absorption apparatus.

[0004] In this method, however, impurities such as aluminum (Al), or iron (Fe) can be dissolved easily with vaporized HF, but impurities of heavy metals such as copper (Cu), and gold (Au), are difficult to dissolve. Therefore, accurate quantitative analysis could not be made for these metals.

[0005] As a means to overcome these shortcomings, the following method of analysis has been devised. In this method, a dissolving solution containing HF and $H_3 O_2$ **(TN: Possibly a typo of $H_2 O_2$)** or a dissolving solution containing HF and HNO_3 is dripped on the surface of semiconductor substrate. The semiconductor substrate is put in motion so that the dissolving solution makes contact with the surface of substrate. Thus, the impurities contained in the natural oxide film formed on the semiconductor surface and the impurities adhered to the surface of semiconductor substrate are dissolved. The dissolving solution is collected to measure the type and quantity of the impurity contained with a flameless atomic absorption apparatus.

[0006] When a dissolving solution containing HF and $H_2 O_2$ is used, the concentration of $H_2 O_2$ must be made sufficiently high to dissolve the heavy metal impurity such as Cu into the dissolving solution in order to accurately detect it. However, when the concentration of $H_2 O_2$ is made high, the surface of semiconductor substrate becomes hydrophilic. Consequently, it becomes difficult to roll the dissolving solution. Additionally, the collection of dissolving solution to make the measurement also becomes difficult. These problems have hindered the improvement of the accuracy of analysis results.

[0007] In addition, when a dissolving solution containing HF and HNO_3 is used, the concentration of HNO_3 must also be increased to accurately detect the Cu. However, when the concentration of HNO_3 is increased, etching occurs reaching the interior of the semiconductor substrate. This dissolves the impurities in the interior of the semiconductor substrate. Therefore, it has been unsuitable for the analysis of the type and quantity of impurities adhered to the surface of semiconductor substrate.

[0008]

[Problems to Be Solved by the Invention] As described above, the method of conventional technology using a dissolving solution containing HF and H_2O_2 causes the semiconductor substrate to become hydrophilic, and makes it difficult to roll the solution. The method of using a dissolving solution containing HF and HNO_3 causes etching of the interior of the semiconductor substrate. Consequently, it is difficult by either method, to accurately measure the type and quantity of the impurities adhered to the semiconductor substrate surface. The purpose of this invention is to present a method that solves the problems described above, and analyzes the type and quantity of impurity adhered to the semiconductor substrate surface with high degree of accuracy and sensitivity.

[0009]

[Means to Solve the Problems] In order to accomplish the purpose stated above, the method of analyzing the impurities on the semiconductor substrate surface of this invention is characterized by the following processing steps. The method comprises a processing step to create a dissolving solution containing HF and O_3 on the surface of semiconductor substrate, and a processing step to roll the dissolving solution on the semiconductor substrate surface to make contact. It also comprises a processing step to analyze said dissolving solution to measure the type and quantity of the impurity adhered to the semiconductor substrate surface.

[0010] Additionally, the dissolving solution containing HF and O_3, mentioned above, is characterized by being created by mixing gaseous O_3 with either an aqueous solution of HF or vaporized HF.

Additionally, the dissolving solution containing HF and O_3, mentioned above, is characterized by being created by mixing aqueous solution of O_3 with either an aqueous solution of HF or vaporized HF.

[0011] In addition, the method of analyzing impurity on the semiconductor substrate surface of this invention is characterized by the following composition. The method comprises a processing step to drip dissolving solution containing HF and O_3 on the surface of semiconductor substrate. It also comprises a processing step to roll the dissolving solution on the semiconductor substrate surface to make contact, and a processing step to measure the type and quantity of the impurity adhered to the semiconductor substrate surface.

[0012]

[Operation] In the analyzing method of this invention, a solution containing HF and O_3 is rolled on the surface of the semiconductor substrate to make contact so that the impurities present on the surface of semiconductor substrate is dissolved into the dissolving solution.

[0013] The process of this dissolving can be inferred to take place as follows. First, the dissolving solution containing HF and O_3 efficiently forms an oxide film on the surface of the semiconductor substrate by the oxidation power of O_3. The impurities adhered to the surface of the semiconductor substrate is incorporated into the oxide film. However, the oxidation power of O_3 deteriorates rapidly. Consequently, the dissolving power of HF becomes stronger after a short time, and dissolves the oxide film, as the oxidation power is dissipated. In addition, the dissolving solution containing HF and O_3 has a slower rate of etching the semiconductor substrate than the dissolving solution containing HF and HNO_3. Consequently, the dissolving solution containing HF and O_3 can dissolve the impurities on the semiconductor substrate surface efficiently without dissolving the impurities contained in the interior of the semiconductor substrate.

[0014]

[Embodiment] The embodiment of the invention will be explained in the following referring to the figures. The first embodiment of the invention is shown in Figure 1. An apparatus is shown that realizes a method of analyzing impurities adhered to the surface of semiconductor substrate by creating a dissolving solution, by supplying vaporized HP and gaseous O_3, and analyzing the impurities adhered to the semiconductor substrate surface. The apparatus comprises a table 13 that holds a semiconductor substrate, composed of Si as raw material, in a chamber 11, as shown in Figure 1. It also comprises, a driving mechanism 14 that provides motion to the semiconductor substrate 12, a line 15 that supplies vaporized HF, and a line 16 that supplies gaseous O_3. When the measurement is made, the semiconductor substrate, composed of Si as raw material, is placed on the table 13 in the chamber 11, and vaporized HF and gaseous O_3 is supplied onto the surface of the semiconductor substrate 12.

[0015] The vaporized HF and gaseous O_3 reacts chemically after being exposed to air, and a dissolving solution 17 is created after being liquefied. Next, the semiconductor substrate 12 is rotated by the driving mechanism 14, while shifting the horizontal surface, so that the solution 17 is rolled around on the semiconductor substrate 12 to make contact. The impurities contained in the natural oxide film formed on the surface of semiconductor substrate 12, and the impurities adhered to the surface of semiconductor substrate 12 are incorporated into the dissolving solution 17.

[0016] The following events are inferred to take place in this dissolving process. First, the dissolving solution 17 containing HF and O_3 efficiently oxidizes the surface of the semiconductor substrate 12 by the oxidizing power of O_3 contained in the dissolving solution 17. The oxide film formed contains the impurities adhered to the surface of the semiconductor substrate 12. However, the oxidizing power of O_3 contained in the dissolving solution 17 deteriorates rapidly, giving way to the HF's dissolving power of the oxide film, as time elapses. The natural oxide film and the oxide film formed are dissolved. Then, the dissolving solution 17 is collected with a pipette, and measurement is made for the type and quantity of the impurities contained with a flameless atomic absorption apparatus. Alternatively, the dissolving solution 17 can be dried on the semiconductor substrate 12 without being collected, and analyzed with a total reflection X-ray analysis.

[0017] The results of experiment performed actually using a dissolving solution containing HF and O_3 will be explained, particularly noting the (1) solubility of Cu which is the heavy metal impurity, and (2) the etching rate of the Si substrate.

[0018] (1) An Si substrate on which 6 x 10^{12} (atoms / cm²) of Cu is adhered is soaked for three minutes under normal temperature in a dissolving solution containing 0.2 % concentration of HF and 1 to 10 ppm concentration of O_3. The dissolving solution dissolved approximately 4.00 to 5.90 (x 10^{11} atoms / cm²) of Cu. On the other hand, when an Si substrate with identical condition is soaked in a dissolving solution containing 0.2 % concentration of HF and 0.1 to 10% concentration of H_2O_2, approximately 5.70 to 5.95 (x 10^{12} atoms / cm²) of Cu was dissolved. Clearly, the dissolving solution containing HF and O_3 recovers Cu more efficiently than in the past. **(TN: Possible typos in the figures (?))**

[0019] (2) The etching rate of Si substrate by the dissolving solution containing approximately 0.05 to 0.5 % concentration of HF and approximately 2 ppm concentration of O_3 is approximately 3 to 17 (A / min). The etching rate of Si substrate by a solution containing approximately 0.02 to 4% concentration of HF and approximately 68% concentration of HNO_3 is approximately 100 to 6000 (A / min). The etching of Si substrate can be suppressed more than the conventional method by using a solution containing HF and O_3.

[0020] Next, the second embodiment will be explained. The second embodiment of this invention is shown in Figure 2. An apparatus that realizes a method of analyzing impurities adhered to the surface of semiconductor substrate where a dissolving solution is created by supplying aqueous solution of HF and aqueous solution of O_3 is shown. As shown in Figure 2, the apparatus comprises a table 23 that holds the semiconductor substrate 22, composed of Si as raw material, placed in a chamber 21. It also comprises, a driving mechanism 24 that provides motion to the semiconductor substrate 22, a line 25 supplying aqueous solution of HF, and a line 26 supplying aqueous solution of O_3.

[0021] When a measurement is made, the semiconductor substrate 22 is placed on the table 23. The aqueous solution of HF and aqueous solution of O_3 is supplied onto the surface of semiconductor substrate 22 to create a dissolving solution 27. Next, the semiconductor substrate 22 is rotated by a driving mechanism 24 while shifting the horizontal surface, so that the dissolving solution 27 is rolled around on the semiconductor substrate 22 to make contact. The impurities contained in the natural oxide film formed on the surface of the semiconductor substrate 22 and the impurities adhered to the surface of the semiconductor substrate 22 are incorporated into the dissolving solution 27. Then, the dissolving solution 27 is collected by a pipette, and the type and quantity of the impurities are measured by a flameless atomic absorption apparatus. Alternatively, the solution 17 can be dried on the semiconductor substrate 12 without being collected, and analyzed with a total reflection X-ray analysis.

[0022] In the two embodiments described above, the dissolving solution containing HF and O_3 has been created on the surface of the semiconductor substrate 22. However, the dissolving solution 27 containing HF and O_3 can be prepared ahead of time, and dripped onto the semiconductor substrate 22 to make measurement.

[0023] In the two embodiments described above, the semiconductor substrate analyzed were composed of Si. However, the application of this invention is not limited to semiconductor substrates composed of Si, any other semiconductor, such as chemical compound semiconductor can be used. Additionally, in the first and second embodiments shown above, the line supplying vaporized HF or aqueous solution of HF, and the line supplying gaseous O_3 or aqueous solution of O_3 are not limited to the number and positions described in Figures 1 and 2. Any other configuration producing the dissolving solution 27 would be acceptable.

[0024] Additionally, as for the timing of supplying vaporized HF or aqueous solution of HF, and gaseous O_3 or aqueous solution of O_3, the dissolving solution 27 can be created more efficiently when both substances are supplied simultaneously. It is effective in producing the dissolving solution 27 more quickly. When vaporized HF or aqueous solution of HF is supplied first, the vaporized HF or aqueous solution of HF dissolves the impurities on the surface of the semiconductor substrate 22, exposing the surface of the semiconductor substrate

22. Since the semiconductor substrate surface 22 itself shows hydrophobic property, the effect of making the solution easier to roll around on the surface of semiconductor substrate 22 can be obtained.

[0025] In the creation of dissolving solution 27, an example of supplying both HF and O_3 in gaseous state, and an example of supplying both in aqueous solutions were cited in the embodiments. However, the dissolving solution 27 can be created by supplying either one of the substances in gaseous state and the other in aqueous solution. Additionally, a method of preparing the dissolving solution 27 containing a mixture of HF and O_3 ahead of time, and dripping it onto the surface of the semiconductor substrate 22 would be acceptable. In other words, so long as a substance containing HF and O_3 is created on the surface of the semiconductor substrate 22, the process of its creation does not matter.

[0026] However, O_3 decomposes rapidly in aqueous solution. Consequently, the oxidizing power of O_3 diminishes in relatively short time. Therefore, it is preferable to prepare the aqueous solution of O_3 immediately before the measurement is made. When a solution 27 containing a mixture of HF and O_3 is prepared ahead of time, and dripped onto the surface of semiconductor substrate 22, it is also preferable to prepare it immediately before the measurement is made.

[0027] As for the means of rolling the dissolving solution 27 on the surface of semiconductor substrate 22, it is not limited to the method described in the embodiment. For example, there is a method where a jig resembling a dropping pipette, holding the dissolving solution 27, is placed in contact with the surface of the semiconductor substrate 22. Then, as the semiconductor substrate 22 is rotated, the dropping pipette is simultaneously moved horizontally, dissolving the impurities attached to the surface of the semiconductor substrate 22 into the dissolving solution27.

[0028] The measurement method is not limited to the analysis method using a flameless atomic absorption apparatus or a total reflection X-ray analysis. Any method capable of determining the type and quantity of the atoms of impurities dissolved in the dissolving solution 27 would be acceptable. For example, mass spectrometry analysis by means of inductive coupling plasma (ICP) may be used.

If it is necessary to collect the dissolving solution 27, the semiconductor substrate 22 can be tilted to collect the dissolving solution 27. The means of accomplishing the collection does not matter.

[0029]

[Effects of the Invention] The method of analyzing the impurities on the surface of semiconductor substrate of this invention can measure the type and quantity of the impurities adhered to the surface of semiconductor substrate with high degree of accuracy and sensitivity.

[Brief Explanation of the Drawings]

[Figure 1] This is the first embodiment of the invention. An apparatus that realizes a method of analyzing the impurities adhered to the surface of semiconductor substrate, utilizing a dissolving solution created by supplying vaporized HF and gaseous O_3 is shown.

[Figure 2] This is the second embodiment of this invention. An apparatus that realizes a method of analyzing the impurities adhered to the surface of semiconductor substrate, utilizing a dissolving solution created by supplying aqueous solution of HF and aqueous solution of O_3 is shown.

[Explanation of Symbols]

11, 21. Chamber
12, 22. Semiconductor substrate
13, 33. Table
14, 24. Driving mechanism
15. Supply line of vaporized HF
16. Supply line of gaseous O_3
17, 27. A drop of dissolving solution of HF and O_3
25. Supply line of aqueous solution of HF
26. Supply line of aqueous solution of O_3

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[Figure 1]

[Figure 2]